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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08F 2/46, 2/50, 4/00, 4/40 — A1

(11) International Publication Number: WO 97/45458

(43) International Publication Date: 4 December 1997 (04.12.97)

(21) International Application Number: PCT/US96/15464

(22) International Filing Date: 26 September 1996 (26.09.96)

(30) Priority Data:
08/553,679 26 September 1995 (26.09.95) US

(60) Parent Application or Grant
(63) Related by Continuation
US 08/553,679 (CIP)
Filed on 26 September 1995 (26.09.95)

(71) Applicant (*for all designated States except US*): UV COATINGS LIMITED [US/US]; 23205 Mercantile Road, Beachwood, OH 44122 (US).

(72) Inventor; and
(75) Inventor/Applicant (*for US only*): SOKOL, Andrew, A. [US/US]; 23205 Mercantile Road, Beachwood, OH 44122 (US).

(74) Agent: WEINTRAUB, Arnold, S.; Suite 444, 30200 Telegraph Road, Bingham Farms, MI 48025 (US).

(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: FINISHING COMPOSITION WHICH IS CURABLE BY UV LIGHT AND METHOD OF USING SAME

(57) Abstract

A sprayable coating composition is formulated using one or more acrylates and one or more photoinitiators which act to polymerize the composition when exposed to ultraviolet light. Because of the use of low molecular weight monomers or oligomers, the composition is essentially free of volatile organic solvents and therefore evaporative emissions in curing are substantially eliminated. The composition includes a non-reactive diluent to enable a wider range of viscosities.

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FINISHING COMPOSITION WHICH IS CURABLE BY UV LIGHT AND METHOD OF USING SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

This Application is a continuation-in-part-application of co-pending U. S. Patent Applications Serial No. 08/553,679, filed September 26, 1995, for "Finishing Composition Which Is Curable By UV Light and Method of Using Same" which, in turn is a continuation-in-part of co-pending U. S. Patent Application Serial No. 08/038,518, filed March 29, 1993, of the same title, now U.S. Patent No. 5,453,452, which was a continuation application of U.S. Patent Serial No. 07/701,442, now abandoned, the disclosures of which are hereby incorporated by reference.

Background of the Invention

Field of the Invention:

The present invention relates to a substantially volatile organic solvent-free coating composition which is curable by the application of ultraviolet light thereto, and a method of using the composition. More particularly, the present invention relates to such a coating composition which includes a polymerizable compound which includes at least one acrylate-containing compound and a photoinitiator which initiates a polymerization reaction in the composition when it is exposed to ultraviolet light.

Prior Art:

In the above-referred to co-pending application as well as in the issued patent, there is disclosed a two-part coating composition curable by exposure to ultraviolet light or other energy source and which, generally, comprises a mixture of acrylates and a photoinitiator. The major predicate of the prior inventions is the elimination of volatile organic solvents and hazardous air pollutants (HAPS) from their respective systems, while still being sprayable. With the public desire for the elimination of volatile organic solvents from coating systems, necessarily, the inventions of the related applications provide a major improvement in the art, especially from a health and environmental standpoint. However, it is to be appreciated that as a consequence of the elimination of the volatile organic solvents the viscosity of the composition must remain within a certain controlled range in order for the composition to be sprayable. It would be most desirable to have the ability to incorporate into such systems non-volatile as well as minor amounts of volatile organic solvents or reactive and/or non-reactive diluents so that the viscosity of the resulting composition(s) can be widened. Furthermore, the incorporation of the solvent or diluent affords the ability to easily include other components into the coating composition, such as pigments and other coloring agents.

It is to this to which the present invention is directed.

SUMMARY OF THE INVENTION

The present invention provides an improved sprayable coating composition which cures very quickly upon exposure to sunlight, ultraviolet light, as well as upon exposure to electron beams or other suitable energy source. The composition of the present invention is made up predominantly of solids and is, preferably, substantially free of volatile organic solvents.

A coating composition in accordance with the present invention, generally, comprises:

from about 60 to about 99.9 percent by weight, based on the total weight of the composition, of a polymerizable compound which comprises at least one acrylate;

from about 0.5 to about 15 percent by weight, based on the total weight of the composition, of a photoinitiator which initiates a polymerization reaction in the composition when it is exposed to the requisite energy source; and

from about 0 to about 40%, by weight, based on the total weight of the composition, of a non-volatile solvent.

The present invention further contemplates the inclusion of a pigment or other visual effect adjuvant into the composition. Where used the adjuvant is present in an amount ranging from about 0.01% to about 95%, by weight, based on the total weight of the composition.

The polymerizable compound may be selected from the group consisting of urethane acrylates, polyester acrylates, monoacrylates, diacrylates, triacrylates, polyacrylate and the like, and mixtures thereof.

Where electron beam energy is used to initiate the polymerization, the photoinitiator may be eliminated; and

For a more complete understanding of the present invention, the reader is referred to the following detailed description section, which should be read in conjunction with the accompanying examples. Throughout the following description and in the examples, all parts are intended to be by weight, absent indications to the contrary.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In a first aspect hereof, the present invention provides a sprayable coating composition, which is substantially free of volatile organic solvents and which is especially useful for coating wood, metal, stone or concrete or plastic articles. The composition may be made up either as an opaque or a transparent coating composition. The

composition hereof is especially advantageous, as contrasted with the known coating compositions, in that it does not generate any significant organic volatile evaporative emission component during the curing process , while enabling the incorporation of a non-volatile organic solvent thereinto. Curing is effected by a rapid polymerization reaction which is initiated by a photoinitiator component of the composition when it is exposed to an energy source, such as sunlight, ultraviolet light, or other natural or artificial ultraviolet light. Alternatively, and as discussed below, electron beam energy can be used to polymerize the acrylate. Substantially, the entire composition remains in place on the substrate during and after curing.

As noted, above, the coating composition of the present invention, generally, comprises:

from about 60% to about 99.9%, by weight, based on the total composition weight, of a polymerizable compound which comprises an acrylate;

from about 0 to about 40%, by weight, based on the total weight of the composition of a non-volatile solvent or diluent; and

from about 0.1 to about 15 percent, by weight, based on the total composition weight, of a photoinitiator which initiates a polymerization reaction in the composition when it is exposed to ultraviolet light.

Preferably, the composition hereof includes from about 68 to about 84.9 percent of the polymerizable compound, from about 5% to about 25% of the solvent, and from about 0.1 to about 7 percent of the photoinitiator, by weight.

In a preferred embodiment hereof, the coating composition hereof comprises 68 to 84 percent of a first triacrylate 15 to 25 percent of a second monoacrylate, and 0.1 to about 7 percent of the photoinitiator.

Amongst the useful non-reactive or non-volatile diluents include, for example, water; organic diluents, such

as ketones, alcohols, ethers, petroleum distillates, hydrocarbon solvents, butylcellosolve, and the like, as well as mixtures thereof.

Among the useful ketones are acetone methyl ethyl ketone and the like; useful alcohols include, alkanols, diols, triols, and the like, including methyl alcohol, ethyl alcohol, butane diol, trimethylolpropane, glycerol and the like.

Useful ethers include, for example, vinyl ether, ethyl ether, methyl ether and the like. Useful hydrocarbon solvents include benzene, tolene, hexane, heptane and so forth, as well as mixtures thereof.

Other useful solvents or diluents include liquid triacrylates, polyesters, esters, and the like. The incorporation of the diluent enables the viscosity of the composition to be lowered to a range of from about 0.1cps to about 300cps at 25°C. Likewise, by virtue of the presence of the diluent the viscosity, when used with the appropriate photoinitiator, can range upward of to about 100,000cps. Thus, the viscosity can range from about 0.1cps to about 100,000cps at 25°C and still remain sprayable.

Within the broad class of non-reactive diluents, it is preferred to employ water, alcohols, ketones or ethers, as well as mixtures thereof (and most, preferably, acetone).

The polymerizable compound may be selected from the group consisting of monoacrylates, diacrylates, triacrylates, polyacrylates, urethane acrylates, polyester acrylates, and the like, as well as mixtures thereof. The polymerizable compound, preferably, includes a mixture of acrylates. Suitable compounds which may be used in the practice of the present invention include but are not limited to, trimethylolpropane triacrylate, alkoxylated trimethylolpropane triacrylate, such as ethoxylated or propoxylated trimethyolpropane triacrylate, 1,6-hexane diol diacrylate, isobornyl acrylate, aromatic and aliphatic urethane acrylates, vinyl acrylates, epoxy acrylates,

ethoxylated bisphenol A diacrylates, trifunctional acrylic ester, unsaturated cyclic diones, polyester diacrylates, and mixtures of the above compositions.

The photoinitiator which is used in the composition of the present invention may be of the free radical or cationic type. A combination of photoinitiators may be used. Photo-initiators which are suitable for use in the practice of the present invention include, but are not limited to, 1-phenyl-2- hydroxy-2-methyl-1-propanone, oligo{2-hydroxy-2 methyl-1-[4- (methylvinyl)phenyl] propanone}, 2-hydroxy 2-methyl 1-phenyl propan-1 one, bis (2,6-dimethoxybenzoyl)-2,4,4- trimethylpentyl phosphine oxide, 1-hydroxycyclohexyl phenyl ketone and benzophenone as well as mixtures thereof.

Other useful initiators include, for example, bis(n,5,2,4- cyclopentadien -1-yl)-bis[2,6 -difluoro-3-(1H-pyrol-1-yl) phenyl] titanium and 2-benzyl -2-N,N-dimethyl amino -1- (4-morpholinophenyl) -1- butanone. Both of these compounds are commercially available and sold by CIBA under the names IRCACURE 784 DC and IRGACURE 369, respectively.

These latter two initiators enable visible sunlight cure and high pigment loading cure which is discussed further hereinbelow.

Still other useful photoinitiators include, for example, benzophenone, 2-methyl -1- [4(methylthio) -2-morpholinopropan]- 1-one, 4-(2-hydroxy) phenyl -2-hydroxy -2-methylpropyl) ketone, 1-hydroxy cyclohexyl phenyl ketone benzophenone, (n-5,2,4- cyclopentadien -1-yl) [1,2,3,4,5, 6-n)- (1-methylethyl) benzene]-iron(+) hexafluorophosphate (-1), 2,2 -dimethoxy -2-phenyl-1-acetophen-one 2,4,6-trimethyl benzoyl-diphenyl phosphine oxide, benzoic acid, 4-(dimethyl amino) -ethyl ether, as well as mixtures thereof.

Yet, other useful photoinitiators include those sold by Sartomer under the name ESACURE, including the EB3,

KB1, TZT, KIP 100F, ITX, EDB, X15 and KT37 ESACURE photoinitiators, these all being commercially available.

A preferred coating composition hereof comprises 65 to 85 percent propoxylated trimethylolpropane triacrylate, 15 to 25 isobornyl acrylate, and 0.1 to about 7 percent of a photoinitiator which is a mixture of bis (2,6-dimethylbenzoyl) 2,4,4-trimethylpentyl phosphine oxide and 2-hydroxy- 2-methyl -1-phenyl-propan-1-one, sold commercially by CIBA-GEIGY under the Mark IRGACURE 1700 or IRGACURE CGI1700. This photoinitiator enables both high pigment loading as well as sunlight cure.

Thus, a preferred pigmented formula in accordance with the present invention comprises 50 to 70 percent of the triacrylate, 1 to 30 percent of the isobornyl acrylate, from about 5 to about 30 percent of the diluent, and, 0.1 to 50 percent pigment solids, and 0.1 to 7 percent of the IRGACURE 1700 photoinitiator.

It is to be appreciated that the present invention may be cured by natural sunlight, by medium pressure mercury arc lights, or by long wave ultraviolet light depending on the photoinitiator package used. Also, as noted, the polymerization may be electron beam initiated, thus, omitting the need for the photoinitiator.

Likewise, and as noted hereinabove, depending on the photoinitiator package, high pigment loading is available. Pigment loading up to about 95%, by weight, of the composition is possible, although not necessarily desirable because of economic reasons.

Where pigment loading is desired the skilled practitioner is able to choose from a wide variety of pigments and other visual effect materials including phosphorescent compounds, depending on the oil absorption factors. Useful pigments and other visual effect materials, include both organic and inorganic dyes, both natural and synthetic, as well as other naturally occurring materials, organic and inorganic pigments, etc. Useful compounds include, for example, carbon black; titanium dioxide;

phthalocyanate; azo dyestuffs; metal oxides, such as iron oxide; synthetic coloring agents, such as nitrosyl amines, benzoyl compounds, and the like; for pearlesence ground mica may be incorporated. Also, polycarbonates, naturally occurring dyes, chromates, molybdates and the like, as well as mixtures thereof may be included herewithin. The pigment and/or visual effect material may be ground and, then, admixed with the coating composition simply by stirring or milling it into the composition or otherwise dispersing it thereinto the like. However, where a high viscosity is associated with the coating composition the composition may have to be heated to a temperature of up to about 100°C, in order to incorporate the pigment and/or visual effect material into the composition.

Where the pigment is present, typically, is it employed in an amount ranging from about 0.1% to about 80%, although up to about 95% is achievable. Preferably, the compound is present in an amount ranging from about 1% to about 50%.

The composition of the present invention is a significant improvement over the prior art coating compositions because of the fact that it does not contain any significant organic solvent which must be evaporated before curing is complete and its attendent environmental problems. Rather, the present invention includes low molecular weight polymerizable monomers and/or oligomers which are polymerized in place upon exposure to ultraviolet light. Therefore, the composition of the present invention is much less hazardous to the environment than the previously available compounds which included organic solvents which had to be evaporated into the atmosphere in order to cure the finish. To control pre-polymerization viscosity for sprayability, dipping or other means of application, a low molecular weight mono or di-acrylate is used, preferably, as one component of the present composition.

Possible methods of application include spraying, brushing, curtain coating, dipping, and rolling.

Because of the quickness of curing of the present composition, the formulation can be applied in repeated cycles.

The composition of the present invention has the ability, under proper conditions, to be applied, cured, and sanded or burnished within the span of one minute and is then ready for repeated cycles. As such, five or ten coats can be applied in as many minutes.

The composition has the ability to control viscosity by the use of low molecular weight monomers which take the place of organic solvents but which also participate and contribute to final polymer properties. As viscosity can be controlled, the formulation can be used as a stain or sealant. When used on porous substrates such as wood, concrete or SMC speed of penetration is a direct function of viscosity. Therefore, by controlling the viscosity of the material, depth and speed of penetration before curing can be controlled. On curing, the material polymerizes in and about the substrate providing adhesion thereto. The preferred viscosity of the composition hereof is from about 2 centipoise to about 1200 centipoise to about 1500 at 25°C and preferably from about 2 to about 1200 centipoise at 25°C.

Also, it is possible to tailor the properties of the present coating composition, depending on its intended use. Thus, both silicone-based and halogenated organic-based surfactants can be incorporated hereinto.

Where water repellancy or adhesion to silica-type substrates such as glass, concrete, stone and the like is a desired a silicone-based surfactant, such as a siloxane or silane, may be admixed herewith. Although inorganic compounds maybe used as well; typically, the silicone is employed as a silane, corresponding to the formula:

R-Si-OR1

where R and R1 are substituted or unsubstituted linear alkyl or alicyclic having from about 1 to 4 carbon atoms in the alkyl portion thereof.

Some useful silanes are for example, methyltrimethoxy silane, butyltrimethoxy silane, chlorpropyltrimethoxy silane, glycidyl oxide methoxy silanes, and the like, as well as mixtures thereof. Preferred compounds are glycidoxy methoxy silanes, such as that sold by Dow Corning under the name SILWET RC-73. Other useful wetting agents include the siloxanes corresponding to the formula:

(Si-O-Si)

such as the polydimethyl siloxane fluids. A preferred siloxane is methyloxysiloxane.

Generally, the silicone surfactant is used in an amount, by weight, based on the total composition, ranging from about 0.0001 percent to about 5.0 percent.

Halogenated surfactants are used to achieve high gloss and mar resistance. Useful halogenated surfactants include fluoroaliphatic polymeric esters and alkyl alkoxylates. These halogenerated adjuvants are used in the same amounts as the silicone surfactants:

Also, to promote adhesion to metals, an acrylate or methacrylate ester derivative surfactants may be used.

Although the present invention has been described herein with reference to preferred compositions thereof, the foregoing description and examples are intended to be illustrative, and not limitative. Many modifications of the present invention will occur to those skilled in the art. All such modifications which fall within the scope of the following claims is intended to be within the scope and spirit of the present invention.

Having, thus, described the invention, what is claimed is:

CLAIMS

1. A sprayable, substantially solvent-free coating composition for applying to a substrate, comprising:

from about 60 to about 99.9 percent by weight, based on the total composition weight, of a polymerizable compound which comprises a mixture of acrylate, the acrylate mixture comprising a first acrylate and a second acrylate which has a lower molecular weight as compared to the first acrylate, the second acrylate being present in the composition in a amount effective to control pre-polymerization viscosity to a value in a range from about 2 centipoises to about 1500 centipoises at 25°C to facilitate ease of application,

from about 0 to 40%, by weight, based on the total weight, of a non-reactive diluent.

from about 1 to about 15 percent by weight, based on the total composition weight, of an photoinitiator which initiates a polymerization reaction in the composition when it is exposed to ultraviolet light; and

wherein the composition is curable upon exposure to a source of energy without requiring evaporation of a non-volatile organic solvent therefrom.

2. The composition of Claim 1, wherein the polymerizable compound is selected from the group consisting of polyester acrylates, urethane acrylate, monoacrylates, diacrylates, triacrylates, polyacrylates, and mixtures thereof.

3. The composition of Claim 1, wherein the photoinitiator is selected from the group consisting of 1-phenyl-2-hydroxy-2-methyl-1-propanone, oligo{2 hydroxy-2 methyl-1-[4-(methylvinyl)phenyl]propanone}, 2 hydroxy 2-methyl 1-phenyl propan-1-one, 1-hydroxycyclohexyl phenyl ketone, benzophenones, thioxanthones, camphorphenones, cationic photoinitiators and mixtures thereof.

4. The composition of Claim 1, further comprising from about 0.01% to above 90%, by weight, of a pigment or dye.

5. The composition of Claim 2, wherein the polymerizable compound is selected from the group consisting of trimethylol propane triacrylate, trimethylolpropane triacrylate, 1,6-hexane diol diacrylate, aliphatic urethane acrylates, vinyl acrylates, epoxy acrylates, ethoxylated bisphenol A diacrylate, trifunctional acrylic ester, unsaturated cyclic diones, polyester diacrylates, alkoxylated trimethylolpropane triacrylate, isoboronyl diacrylate, vinyl acrylates, and mixtures thereof.

6. The composition of Claim 1 wherein the non-reactive diluent is selected from the group consisting of water, ketones, alcohols including alkanols, diols and triols, alkyl ethers, petroleum distillates, aliphatic alicyclic and aromatic hydrocarbon solvents, butylcellosolve and mixtures thereof.

7. A sprayable, substantially solvent-free coating composition for applying to a substrate, consisting essentially of:

from about 60 to about 99.9 percent by weight, based on the total composition weight, of a polymerizable compound which comprises;

from about 0 to 25% by weight, based on the total weight of a non-reactive diluent;

from about 0.5 to about 15 percent by weight, based on the total composition weight of a photoinitiator which initiates a polymerization reaction in the composition when it is exposed to ultraviolet light; and,

wherein the composition is curable upon exposure to a source of energy without requiring evaporation of a volatile solvent therefrom, the composition being without an inorganic thickener and without a curing agent; and wherein the polymerized compound comprises at least one acrylate of a low

molecular weight in an amount effective to control pre-polymerization viscosity to a value in a range from about 0.1 centipoises to about 100,000 centipoises at 25°C.

8. A method of using a photopolymerizable compound to coat an article of manufacturing, comprising the steps of:

(a) applying a photopolymerizable compound to a surface of the article; the composition consisting essentially of:

(1) the composition of Claim 1;

(b) irradiating the compound which has been applied to the surface with ultraviolet light to initiate a polymerization reaction; and

wherein the compound polymerizes in place on the article substantially without releasing volatile solvents.

9. The method of Claim 7, wherein the article is a porous substrate such that the adhesion is promoted upon polymerization of the composition.

10. The composition of Claim 1, wherein the composition comprises 65 to 85 percent of an alkylated triacrylate, 15 to 25 percent of a monoacrylate and 0.1 to 7 percent of the photoinitiator.

INTERNATIONAL SEARCH REPORT

Int...ational application No.
PCT/US96/15464

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C08F 2/46, 2/50, 4/00, 4/40
US CL :522/42, 75, 81, 103, 182; 427/519
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 522/42, 75, 81, 103, 182; 427/519

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: acrylate, photoinitiator, sprayable

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	US 5,453,451 A (SOKOL) 26 SEPTEMBER 1995, entire document.	1-10
A	US 4,721,734 A (GEHLHAUS et al.) 26 JANUARY 1988.	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search 05 DECEMBER 1996	Date of mailing of the international search report 15 JAN 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer MARK A. CHAPMAN Telephone No. (703) 308-2351

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